Exploiting catalytic chain transfer polymerisation for the synthesis of carboxylated latexes via sulfur-free RAFT

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((Additional Supporting Information may be found in the online version of this article.))

ABSTRACT

We present a systematic study incorporating carboxyl groups into latex particles in order to enhance colloidal stability and the physical properties of the latex. Poly(methacrylic acid-co-methyl methacrylate) (MAA/MMA) were synthesised via the statistical copolymerisation using catalytic chain transfer polymerisation (CCTP). The co-oligomers were in turn successfully utilised as chain transfer agents for the formation of diblock and pseudo triblock copolymers via sulfur-free reversible addition–fragmentation chain transfer polymerisation (SF-RAFT). These copolymers were characterised using ^{1}H NMR, size exclusion chromatography (SEC), Dynamic Light Scattering (DLS), Dynamic Mechanical Analysis (DMA) contact angle telescope-goniometer and matrix-assisted laser desorption/ionization time of flight mass spectroscopy (MALDI-TOF-MS) techniques.

INTRODUCTION

Techniques for incorporating carboxyl groups into polymer latex particles have attracted attention in recent years.[1-4] Latex particles bearing carboxylic functional groups, either at their surface or internally, have numerous applications in medical diagnostics, adhesives, impact modifiers, as well as paper and textile coatings.[1,2,5-8] Water-soluble carboxylic acid containing monomers such as fumaric acid (FA), itaconic acid (IA), acrylic acid (AA) and methacrylic acid (MAA), listed in order of increasing hydrophobicity, are widely used in emulsion polymerization for the synthesis of carboxylated latexes. They are usually incorporated into the latex particle surface, and even in small quantities have been shown to improve colloidal and freeze-thaw stability, and adhesive properties.[1-3,6,7,9,10]

Traditionally, commercial emulsion polymerisations use free radical processes. Free radical polymerisation is a robust, relatively simple to perform, and offers the widest range of monomer compatibility.[11,12] However, is also suffers from a number of disadvantages, as it is prone to side reactions, which can decrease the reproducibility of reactions, and it is not possible to control the end group of polymers or obtain block copolymers, as it is in living radical polymerisation (LRP).[13-17]

Therefore, supplementary mechanisms for monomer sequence control in polymerisations have been studied and investigated. For instance, the development of living polymerisation methods such as ionic

polymerizations, controlled radical polymerisations; catalytic chain transfer polymerisations (CCTP) and ring opening metathesis polymerisation (ROMP), Nitroxide-mediated radical polymerisation (NMP) reversible addition-fragmentation chain transfer polymerization/macromolecular design by interchange of xanthates (RAFT/MADIX) has all aided progress in the field of polymer science, and it is now possible to form polymers with complex microstructures in methods that were unconceivable a few decades ago.[11,17-25 26,27]

Careful monomer selection in the synthesis of the block copolymer provides additional control over the physical and chemical properties of the final latex and its potential applications.[28,29] In particular the glass transition temperature (T_g), which can be controlled by altering the copolymer composition, making it is possible to tailor a product's properties, and enhance its film strength, tackiness or film formation ability. For example, in industry coatings typically use acrylic, polyester, epoxy and urethane, to produce tough products with relatively high T_g (~ 25 to 65 °C).[1,2,4,13,15,30]

Whereas copolymers with methacrylic, styrene and vinyl acetate are used to produce polymers of moderate T_g (0 to 25 °C), which are used for latex paints, textile binders, and adhesives. Low T_g (–55 to –25 °C) polymers, composed of hydrophilic monomers, such as acrylic acid, are used for pressure sensitive adhesive (PSA) applications, which are frequently soft.[7,15,31,32]

The location of the carboxyl group in polymer latex particles, and in the aqueous phase surrounding them, has been extensively studied.[1,2,4,6,7] The location of the acid within the chain is important as it governs the structure of the polymer and, in turn, the stability of the latex formed. The distribution of the acid is influenced by a number factors, such as the reactivity ratio of the monomers, or the partitioning behaviour of the carboxylic acid over the pH range of the reactions.[2] Carboxylic acid monomers are often highly soluble in water. Nevertheless, they will still partition to varying degrees into the organic phase, subject to their relative hydrophobicity.[1,2,6,33] AA, IA, and FA tend to be highly partitioned to the aqueous phase, even at pH levels below their pKa's, and produce significant amounts of water-soluble polymer. With MAA, there is significantly less water-soluble polymer formed, and the MAA containing copolymer is better partitioned towards the particle, especially at low pH.[1,2,33]

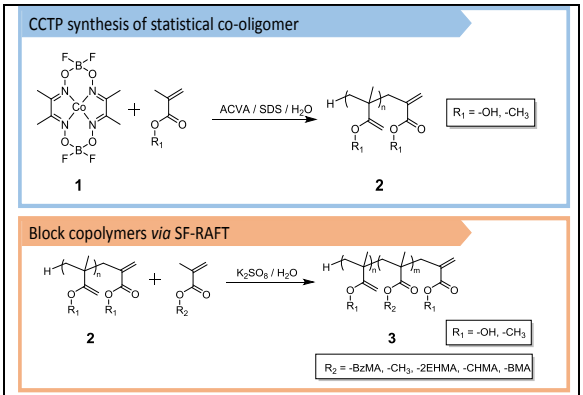


Figure 1: Schematic representation of the Co-mediated CCT and sulfur-free RAFT polymerization of methacrylates.[34-36]

In this work, CCTP was carried out in a seeded emulsion process, with a polystyrene (PS) core, to synthesise vinyl-terminated statistical co-oligomers of MMA and MAA. These were then used *in situ* as chain transfer agents (CTA) for the SF-RAFT polymerisation of various methacrylic monomers, in the formation of di- and pseudo tri-block copolymers. In the synthesis of block copolymers, physical properties such as the glass transition temperature (T_g) of the product can be controlled by the copolymer composition, and so it is possible to tailor a product's properties through the selection of the monomer used to

chain extend from the macro-CTA. Herein we investigate how T_g effects the formation of carboxylated latexes by chain extending with MMA, cyclohexyl methacrylate (CHMA), ethyl methacrylate (EMA), benzyl methacrylate (BzMA), butyl methacrylate (BMA) and 2-ethylhexyl methacrylate (2-EHMA).

RESULTS AND DISCUSSION

Synthesis of statistical co-oligomers via CCTP

This work focused on statistical co-oligomers of MMA (85%) and MAA (15%) as prepared using CCTP in a seeded emulsion. The catalyst used was bis[(difluoroboryl)dimethylglyoximato] cobalt(II), (CoBF) (**1**), which has been previously reported as an effective CTA in the emulsion CCTP of methacrylates.[19,37] This is due to its relative hydrophilicity, which allows it to distribute throughout the continuous phase and diffuse into the polymer particles. The additional consideration in this work was the partitioning of the MAA towards the particles, which are the intended of polymerisation. To help this, we used 4,4'-azobis(4-cyanovaleric acid) as the initiator, which acted to lower the pH of the reaction mixture to approximately 3, where the MAA is protonated and less hydrophilic. It is noted that the k_p of protonated MAA is also higher than in its ionised form.[38] Under these conditions, we synthesised p(MMA-MAA) macromonomers with a range of CoBF concentrations, (*Table 1).*

Reaction	CoBF (ppm)	M_n^{NMR} (g/mol)	M_n^{SEC} (g/mol)	M_w (g/mol)	*Đ*
C1	0	-	57500	221000	3.84
C2	54	5600	5900	9100	1.56
C3	88	3600	3800	5600	1.47
C4	94	2300	2700	3900	1.45
C5	108	1900	2100	3300	1.58
C6	133	1600	1600	2700	1.73

Table1: Data of CCTP co-oligomers with varied CoBF concentration under monomer starved condition.

Reaction C2 of Table 1 shows that by adding 54 ppm of CoBF relative to the monomer concentration, the number average molecular weight (M_n) of the product is reduced from 57 500 to 5 900 g/mol and its dispersity (*Đ*) from 3.84 to 1.56. This higher *Đ* of the reaction without CoBF could be due to the polymer's high viscosity, which has previously been postulated to generate regional differences in monomer concertation due to poor diffusion.[39] Further increases of the CoBF concertation (C2-C6) resulted in lower M_n values for the co-oligomers and comparable *Đ*, (*Table 1)*. Compared with the CCT polymerisation of MMA homopolymer, the apparent chain transfer constant (C_S^E) decreased from 820 to 590 in the synthesis of the co-oligomer (*SI Fig 1.4*), reflecting the lower chain transfer activity of CoBF towards MAA.

We also see good agreement between the M_n values obtained from SEC and NMR, (t*able 1 & SI Fig 1)*. The NMR values are calculated as the ratio of the integrated intensity of a single backbone methyl group proton to the integrated intensity of a proton from the *ω*-vinyl end group. The similarity between these values demonstrated excellent end group fidelity in the macromonomers.

The distribution of MAA throughout the co-oligomers was investigated using MALDI-ToF. We observe distinct distributions of peaks from each DP of the co-oligomer, which are interlinked by peak separations of 100.05 Da and 86.04 Da, approximately the repeat units of MMA (M_o = 100.05) and MAA (M_o = 86.04), respectively, Figure 2A.

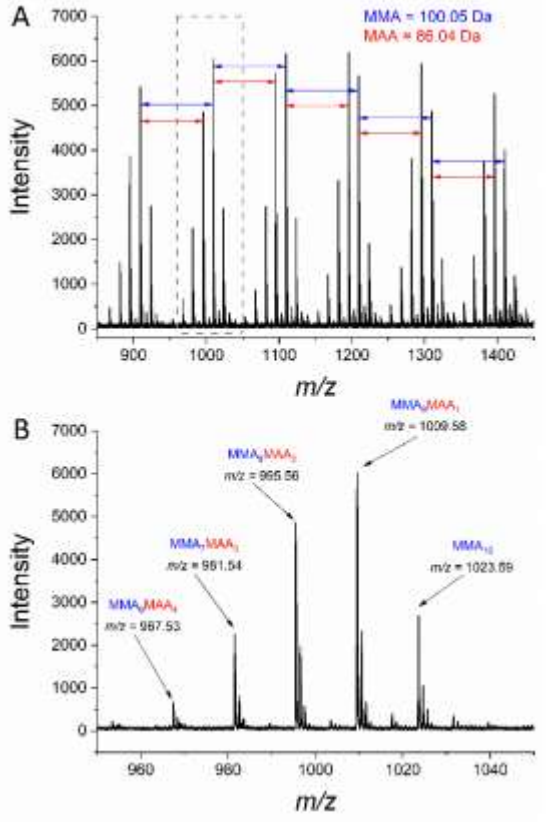


FIGURE 2: MALDI-ToF mass spectrum of the statistical co-oligomers of MMA (85%) and MAA (15%)

The region around DP 10 is expanded in Figure 2B, repeat units are used to determine the make-up of the statistical co-oligomers, with the error being calculated as the difference between the assigned structural mass and the peak mass with minus the cationic mass from the mass spectrum, *(Table 2).*

Peak (m/z)	No. of MMA	No. of MAA	Error (Da)
1023.59	10	0	0.076
1009.58	9	1	0.081
995.56	8	2	0.080
981.54	7	3	0.073
967.53	6	4	0.081

TABLE 2: Analysis of MALDI-ToF spectrum DP 10

The assignments of all observable peaks confirms the expected product of Figure 1, showing the end group fidelity of the ω-unsaturated macromonomer. The pattern of these peaks is repeated throughout the polymer as DP increases (Figure 2). This shows that at all observable degrees of polymerisation, a large fraction of the polymer chains contain both MMA and MAA. For DP 10 of the sample C6 (Table 1) the largest peak coincided with the $PMMA_9MAA_1$ species with an unsaturated vinyl ω-end group. No evidence of fragmentation was observed for any of the co-oligomers.

The error (e_{Da}) in Table 2 was calculated using:

$$e_{Da} = \left| {}^{m}/_{z_{th}} - \left({}^{m}/_{z_{obs}} - m(Na^+) \right) \right| \quad (1)$$

where $\frac{m}{z}_{obs}$ is the observed peak position, $m(Na^+)$ is the mass of a sodium ion and $\frac{m}{z}_{th}$ is:

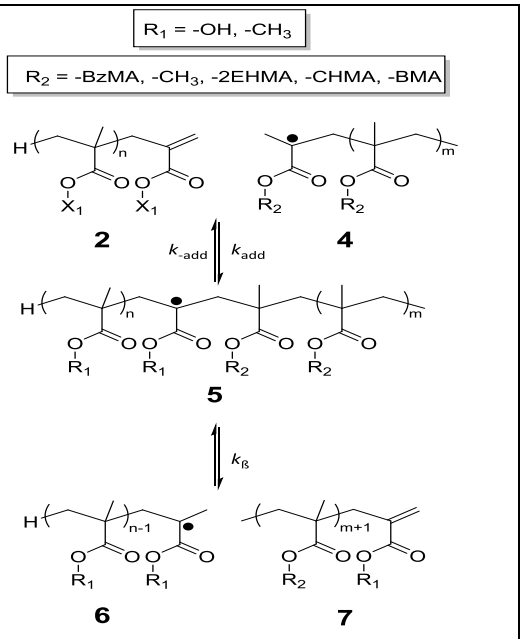
$$\frac{m}{z}_{th} = n(MMA) \cdot m(MMA) + n(MAA) \cdot m(MAA) + m(\omega) \quad (2)$$

where n denotes the number, m is mass and , $m(\omega)$ is the mass of the end groups. The mass of the end groups is functionally 0 due to the vinyl end group, therefore we the number of each monomer units are the only unknowns for each peak. These were solved iteratively, using only positive whole integers for the number of monomer units, to minimize the error and provide the most accurate assignment possible.

Synthesis of di- and pseudo tri-block copolymers *via* SF-RAFT

The mechanism of SF-RAFT has been described previously.[19,34,35,37] Briefly, with reference to Scheme 1, the reaction involves a propagating species (**4**) reacting with a macromonomer/macro chain transfer agent (**2**) to form adduct **5**. This intermediate radical may

then revert to the starting materials or fragment to produce a new propagating species (**6**) and a new macromonomer (**7**). Reaction of **6** with X_2 monomer produces a block copolymer propagating species, which may then react with a macromonomer (**2**, **3** or **7**) to produce a block copolymer (**3**). The final step produces the vinyl terminated ω-chain end to the block copolymer, and so it is itself a macromonomer that can undergo further reaction.



SCHEME 1: Synthesis of block copolymers by SF-RAFT polymersiation.[34-36,40,41]

CCTP co-oligomer with M_n ~ 2500 gmol^{-1} using the date from (*Table 1*) was selected for the synthesis of all di- and pseudo tri-block copolymers, with no need for purification steps. Co-oligomer with 15%MAA and 85%MMA composition was utilised for the synthesis all the di-block co-polymers: since, higher concentration of acid incorporated within the latex resulted in small amount of coagulation (3 – 8 wt%). Furthermore, at high acid concentration (35%MAA and 65%MMA) very small molecular weights polymers with replicative results were not possible to achieve. Moreover, increasing the acid concentration within the latex also increases the particle size of the polymers, whereas 15%MAA-85%MMA composition polymers achieved particle size > 200 nm which insures stable latex with long shelf life (stable after 15 months).

All SF-RAFT polymerisations were performed under monomer starved conditions, this means that the polymer particles are not saturated with monomer, but are being polymerised at an instantaneous conversion of 90% or greater.[37,42] If the monomer feeding rate (i.e. semi-continuous feed) is greater than the polymerisation rate, the reactor will be operating under flooded conditions and control over the copolymer composition would be lost. Therefore, to increase the likelihood that **4** and **6** will interact with a macro-CTA over normal monomer propagation, and also reduce the occurrence of unwanted termination events, such as disproportionation or recombination. All the polymers formed had no coagulation.

To be compatible with emulsion polymerisation, all of the monomers used for chain extension are monomers suitable for conventional emulsion polymerisation and thus relatively hydrophobic, and selected to provide a range of T_g values to the final product. Of those selected, 2-EHMA produced the products with the lowest T_g. Figure 3 shows the SEC traces of the polymers synthesised here. The di-block of 2-EHMA (*DP=25*) had a T_g of 16°C which can be attributed to the fact that first block consisting of very high T_g polymers MAA T_g (228°C) and MMA (105°C) respectively. Tan delta (δ) for 2-EHMA (*DP=25*) was 22°C. The co-oligomer of 15 wt% MAA and 85 wt% MMA by composition had a T_g of 127°C, the onset of the Tg was 109°C whereas the end T_g was 142°C according to DMA with the tan δ same as T_g obtained from storage modulus . For reaction 2-EHMA *(DP=25)*, the onset T_g was 4°C

whereas, the end T_g was 50°C. By addition of the next subsequent block of 2-EHMA (*DP=50*), the T_g increased to 38°C, the onset increased to 17°C, whereas the end T_g remained unchanged. Tan δ for 2EHMA (*DP=50*), increased to 38°C with a small shoulder peak at 13°C SEC revealed that with each subsequent addition of the monomer, a complete shift to higher molecular weight occurred, with DLS confirming an increase in the hydrodynamic diameter of the particles with increasing M_n, SI Table 3, for 2-EHMA (*DP = 25 and 50*) respectively. The low pHs of the emulsions suggest that the MAA of the co-oligomer is protonated, and so we would expect it to be well partitioned towards the particle in these reactions. For reaction BMA (*DP = 25 and DP = 50*) with the next two subsequent block both consisting of BMA monomers the T_g of the di-block was 55°C, the onset obtained was 44°C and the end T_g was 71°C. There was a slight decrease in T_g by the addition of the third block (49°C). However, the final T_g remained similar. Tan δ increased by 6°C for both diblock and trblock copolymers. Of BMA. The SEC and DLS data for copolymerisation of BMA with the macro-CTA (Table 3, *DP = 25 and DP = 50*) gave similar results to 2-EHMA containing polymers.

With the BzMA and EMA block copolymers products with relatively high T_g's were produced (82°C and 104°C, respectively (*DP=25*), and by addition of the third block a slight increase in T_g was observed with BzMA (*DP=50*) T_g~ 86°C, whereas with EMA slight decrease (*DP=50*) T_g~ 95°C. Furthermore, the onset end-point T_g and tan δ remain relatively the same for BzMA at (*DP= 25 & 50*) polymers but for EMA (*DP=25 & 50*) the onset decreased from 92°C to 79°C. However, the end T_g and tan δ remain relatively the same (*SI table 2 & Fig 1.5*), SEC data showed complete shift to a higher molecular weight and increase in particle size was observed with each subsequent addition of the monomer by DLS. In these polymers, we see a less dramatic reduction of *Đ* than in the reactions described above, particularly at higher DPs (Table 3). As the T_g of these polymers is moderately high, the monomers do not partition to the same level of efficiency as with 2-EHMA and BMA, resulting in a higher *Đ* is observed compared to the softer polymers.

Finally, we looked at a diblock of CHMA and MMA, which produce polymers with high T_g's (120°C and 118°C, respectively at (*DP = 25*). The addition of the third block for CHMA *DP = 50* resulted in the T_g staying constant at 118°C and tan δ staying relatively the same. However, with an MMA pseudo tri-block (*DP = 50*) the T_g increased to 128°C with both onset and end T_g also increasing respectively *(SI Table 2).* According to SEC, both (CHMA & MMA derived polymers) exhibit similar behaviors after the formation of the pseudo tri-block. In the di-block formation with MMA (*Table 2*), a decrease in *Đ* is observed by SEC data with a complete shift to higher molecular weight. DLS showed an increase in the hydrodynamic diameter of the particles with increasing M_n. The addition of the third block *Figure 3*, gave an increase in *Đ* with bimodal peaks appearing. This is attributed to the higher T_g of the monomer forming hard polymers and hindering the ability of the monomers to partition between the particles and the aqueous phase. Heuts and co-workers suggested that due to MMA being relatively hydrophilic it does not copolymerise well and SDS addition is required in order to form a stable latex.[4] In this work we have found the addition of plasticisers: o-xylene to MMA diblock and pseudo triblock very effective at reducing the *Đ* significantly and achieving monomodal peaks by addition of the third monomer the *Đ* decreased from 3.21 to 1.39 by addition of the third block

by GPC. Furthermore, o-xylene is a non-polar plasticisers and preferentially plasticised the backbone of the hydrocarbon chains but has less effect on the cluster phase the low density of o-xylene also makes it desirable to use as plasticisers as it is easily removed from the reaction mixture by rotary evaporation *(table 4).*[43,44] Furthermore, if block copolymer with high M_n is desired with low *Đ* for polymers containing MMA monomers it is advisable to add a large block directly via semi continuous addition rather than subsequent addition of the same monomer as this reduces the chain transfer activity of co-oligomer (e.g *DP=50 MMA* rather than *DP=25* and then subsequent addition *DP=50*) *table 3 & 4*.

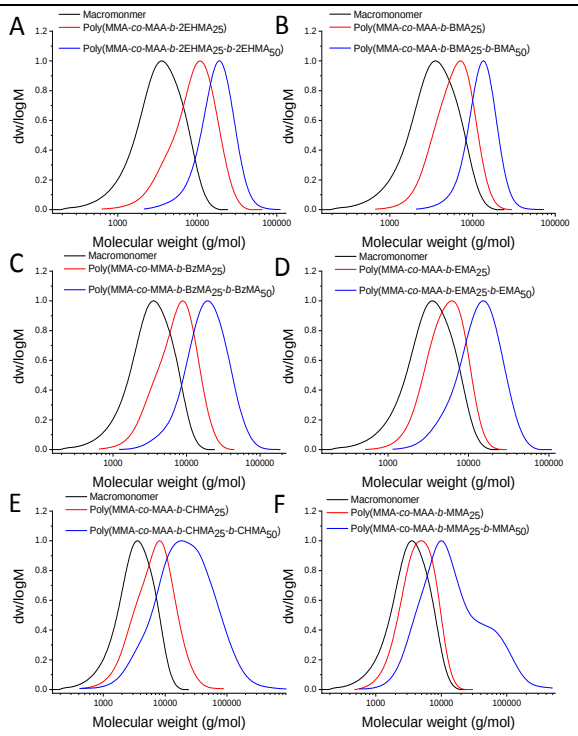


FIGURE 3: SEC of di- and pseudo tri-block copolymers: Red curves are diblock polymers with DP = 25 and blue curves are pseudo tri-blocks DP = 50 with A representing the SEC data for 2-EHMA copolymers, B of BMA copolymers, C of BzMA copolymers, D of EMA copolymers, E of CHMA copolymers and F consisting of MMA copolymers

Reaction	$M_{n,}^{SEC}$ gmol^{-1} (THF)	M_w (gmol^{-1})	*Đ*	$M_{n,th}$ (gmol^{-1})
p(MMA/MAA)	2500	4000	1.63	-
EHMA (DP=25)	7000	10600	1.51	7400
EHMA (DP=50)	15000	19500	1.30	16900
BMA (DP=25)	5000	6700	1.34	6000
BMA (DP=50)	11500	13900	1.20	12100
BzMA (DP=25)	5700	8600	1.49	6900
BzMA (DP=50)	14600	22700	1.56	14500
EMA (DP=25)	4400	6000	1.37	5400
EMA (DP=50)	10600	15300	1.45	10100
CHMA (DP=25)	4900	8800	1.78	6700
CHMA (DP=50)	12100	34900	2.88	10900
MMA (DP=25)	3700	5200	1.42	5000
MMA (DP=50)	8900	28500	3.22	8700

TABLE 3: Properties of di- and pseudo tri-block copolymers of methacrylate derived polymers.

Reaction	$M_{n,}^{SEC}$ gmol^{-1} (THF)	M_w (gmol^{-1})	*Đ*
CHMA-DP=30	6800	12500	1.84
CHMA-DP=30-20wt%-glycerol	6600	11000	1.67
CHMA-DP=30-20wt%-IPA	6400	10200	1.59
Triblock-MMA-DP=50-o-xylene-10wt%	13800	30400	2.20
Diblock-MMA-DP=30-o-xylene-20wt%	4700	6500	1.39
Triblock-MMA-DP=50-o-xylene-20wt%	7100	9800	1.39
MMA-DP=50	5800	7800	1.35

TABLE 4: Properties of di- and pseudo tri-block copolymers of methacrylate derived polymers with plasticizers.

With CHMA a slight increase in *Đ* was initially observed for the formation of diblock (*DP = 25*) and more significant increase in *Đ* was observed for the formation of pseudo tri-block (*DP = 50*), which is attributed to higher T_g of this polymer *(table 3).* The high *Đ* of the higher T_g polymers can be reduced by incorporating plasticisers such as gylycerol and isopropanol (IPA) which is effective at plasticising the ionic domains and reducing melt viscosity which in turn reduces the *Đ* from 3.22 to 2.20 by addition of the third block.[43,44] IPA placticiser is favored over glycerol as it has lower density and easily removed from the reaction mixture by rotary evaporation. Nevertheless, when compared with MMA, the addition of the third block for CHMA resulted in a monomodal molecular weight distribution and a complete shift to a higher molecular weight occurred according to SEC. DLS showed an increase in the hydrodynamic diameter of the particles with increasing M_n for the diblock but for the pseudo triblock the particle sized decreased for reasons not yet known.

Furthermore, for all reactions (*SI Table 3*) the surface zeta potential at pH ~2.5 was -49 mV ±3 which can be attributed to the presence of carboxylic acid and SDS surfactant which was added initially to the reaction mixture for the formation of the co-oligomer. The diblock and pseudo tri-block copolymers contained carboxylic acid functionality monomers and the zeta surface potential are all in the region expected for carboxylated latex.[45,46]

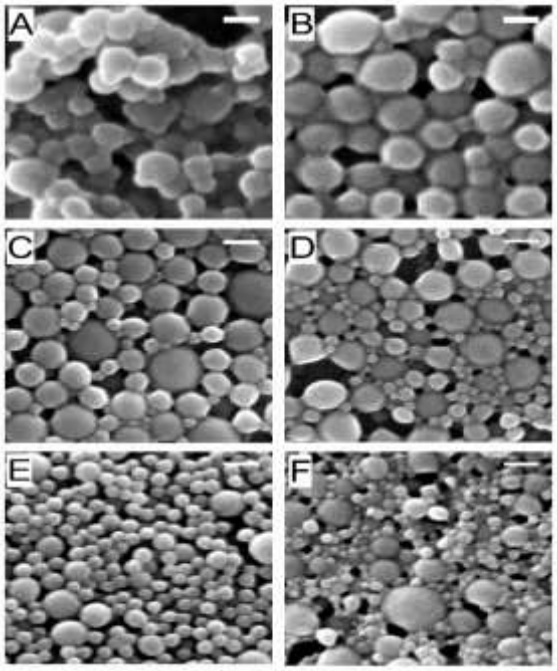


FIGURE 4: SEM micrographs of pseudo tri-block copolymers A representing 2-EHMA, B of BMA, C of BzMA, D of EMA, E of CHMA and F consisting of MMA (scale bar for the SEC data is 200nm)

Each of the latex samples from (*table 3*) were utilised for film formation and their relative wettability was also measured through contact angle measurements. SEM images of the pseudo triblock co-polymers were taken and showed a general monomodal distributions. The lower T_g polymers displayed significant number of particles with uniform monomodal peaks. However, SEM images for low T_g polymers were challenging to obtain due to the heat generated by the electron beam: our observation showed that the size of the particles were uniformed. SEM image F of pseudo PMMA triblock copolymer shows particles with different sizes which explains the bimodal peak according to SEC (*figure 3*). Furthermore, the higher T_g pseudo tri-blocks showed a relatively high PDI values according to DLS and which could have been caused by the (reversible) aggregation of particles in DLS. Nevertheless, it is in agreement

with sulfur free RAFT as the molecular weight of the polymers increases a general increase in dispersity were observed.

Starting with MMA di-block co-polymer (*DP = 25)* with contact angle 48.0°, the addition of the next subsequent block *DP=50* a pseudo tri-block contact angle of 56.7° was obtained, which showed that an increase in the chain length of the polymer resulted in an increase in the hydrophobicity of the polymer by factor of around ~10°. Furthermore, relative to the polymer's of diblock of CHMA (*DP = 25)* and pseudo tri-block (*DP=50*) which were the most hydrophilic polymers according to contact angle measurements: MMA (*DP = 25 & 50*) containing polymers were the next most hydrophilic polymers as their surface tension was the lowest of the polymers from (*table 3*) resulting in a smaller contact angle compared to the other polymers *(SI Fig 4).* Moreover, the polymers with relatively high *Đ's* gave the lowest contact angles (CHMA and MMA at both *DP = 25 & 50*) suggesting that the acid may be residing on the particle surface making the latex's highly hydrophilic. Therefore, the polymer that were relatively hydrophilic had good adhesiveness and wettability properties with high solid surface free energy. The next patch of most hydrophilic polymer was BzMA (*DP = 25* contact angle 58.0°) with next subsequent block also consisting of BzMA monomer with *DP = 50* (contact angle 65.3°) the low contact angle could possibly be attributed to the fact that the benzene ring is delocalised which in turn reduces the surface tension and results in the polymer having similar properties to that of reaction MMA (*DP=25*). The other polymers with increasing alky chain produced results similar to that of the predicted results based on the hydrophobicity of the alkyl chain *DP = 25*; reaction (EMA 62.7°) < (BMA 74.5°) < (2-EHMA 82.6°) and *DP = 50*; reaction (EMA 73.7°) < (BMA 83.0°) < (2-EHMA 92.2°) as the chain length of the polymers increased by the addition of the third block the hydrophobicity of the polymers increased by a factor of around ~10 degrees. The other factor governing the contact angle was the length of the alkyl chain on the R group of the methacrylate monomers as alkyl chain increased the contact angle increased as expected which in turn resulted in poor adhesiveness and wettability properties of the polymer and low solid surface free energy. The initial co-oligomer which were utilised as CTA agent were incredibly hydrophilic and no contact angle measurements could be taken as the droplets spread instantly onto the film; this was expected due to 15wt% of MAA in the latex. However, with reaction with CHMA at both (*DP = 25 & 50*) the results were unexpected as the polymers obtained were highly hydrophilic suggesting that this may be due to higher *Đ's* of the polymers playing a role. As the chain extension occurred with monomers of different hydrophobicity the contact angle measurements correlated well with the fact that as the alky chain length increased the contact angle increased which in turn suggesting that the chains are growing of the co-oligomer and the acid is incorporated well within the latex.

CONCLUSIONS

The versatility of CCT combined with sulfur free RAFT polymerisation has been demonstrated by applying it under emulsion polymerization conditions. Acid rich A blocks with a range of different poly(alkyl methacrylates) have been demonstrated. The conditions were optimised for the formation of the co-oligomers with incorporation of carboxylic acid functionality which in turn were utilised for the formation of well-defined di-block and pseudo tri-block copolymers and by changing the composition of

the monomers added based on hydrophilicity and T_g the latex the morphology of the polymer latex can be altered based of the desired properties.

Furthermore, control over pH in emulsions is essential, as it determines the location of the acid within the polymer latex and it is also believed to play a role in catalyst activity through the rate of hydrolysis of the CCTA at very low pH a slightly higher concertation of catalyst is desired. Moreover, seeded polymerizations can be important for eliminating some of the ambiguity associated with the compartmentalization of the organic phase by controlling the particle numbers and particle size. This also allows for better control over the average number of catalyst molecules per particle which in turn allows the latex to have a long shelf as the particle are usually smaller with incorporation of the seed.

EXPERIMENTAL

See Supporting Information for full experimental details.

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GRAPHICAL ABSTRACT

Ataulla Shegiwal,[1] Alan M. Wemyss,[1] Evelina Liarou,[1] James Town[1] and David M. Haddleton[1]

Exploiting catalytic chain transfer polymerisation for the synthesis of carboxylated latexes via sulfur-free RAFT

We present a systematic study incorporating carboxyl groups into latex particles in order to enhance colloidal stability and the physical properties of the latex. Poly(methacrylic acid-co-methyl methacrylate) (MAA/MMA) were synthesised via the statistical copolymerisation using catalytic chain transfer polymerisation (CCTP). The co-oligomers were in turn successfully utilised as chain transfer agents for the formation of diblock and pseudo triblock copolymers via sulfur-free reversible addition–fragmentation chain transfer polymerisation (SF-RAFT). These copolymers were characterised using ^{1}H NMR, size exclusion chromatography (SEC), Dynamic Light Scattering (DLS), Dynamic Mechanical Analysis (DMA) contact angle telescope-goniometer and matrix-assisted laser desorption/ionization time of flight mass spectroscopy (MALDI-TOF-MS) techniques.